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Introduction

Glassy materials that experience controlled crystallization, usually achieved by a heating process in the presence of nucleating agents, are named glass-ceramics. Due to the good thermomechanical properties and biocompatibility, their major applications are cookware and bone implants. Lately, the control of the crystal size has enabled the development of transparent glass-ceramics with an important role in optical applications.^{1,2} Furthermore, new functionalities can be reached if crystallization is spatially controlled, most of them related to photonic devices. Nevertheless, using the conventional heat treatment, crystallization occurs throughout the whole sample, inhibiting selective growth in previously determined regions. Direct laser writing (DLW) techniques can overcome this issue, since the material properties can be permanently changed with high spatial resolution. For instance, femtosecond laser micromachining has been used to locally modify the optical constants, morphology and oxidation states of transparent materials.^{3,4} Although the production of metallic nanoparticles and single-crystals has been demon-



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Lead oxide is an important glass modifier not only for affecting the chemical and mechanical stabilities of glasses, but also for improving their thermal and optical properties. Since specific properties are associated with the presence of PbO, its crystallization is important to enhance the material performance. Although considerable advances have been achieved regarding the fabrication of glass-ceramic from lead-based glasses, the spatial confinement of the crystallization remains challenging. Direct laser writing (DLW) has been considered an essential technique to overcome this issue, since material properties can be changed in localized and pre-determined regions. Although DLW with femtosecond laser pulses has been widely used for glass processing, its usage for phase transformations and control of the architecture of crystals has not been much exploited. This paper reports the design and control of β -PbO and 3PbO+H₂O crystalline phases in a lead borate glass using fs-DLW followed by chemical etching at room temperature. We demonstrated that the etching in aqueous KOH solution is responsible for the glass crystallization, whereas the grooves produced by fs-laser pulses enable the selective crystallization in a pre-determined 2D pattern. The method described herein is important as it can control phase transformation at the micrometer scale and also permits the growth of lead oxide and lead oxide hydrate phases, which are not achieved by heat treatment. The morphologies of these microcrystals correspond to the structure of the respective compounds, being an octahedral euhedral crystal for $3PbO \cdot H_2O$ and thin sheets for β -PbO crystalline phases.

> strated in glass by DLW with a fs-laser,^{5,6} phase transformations have not been much exploited.

> Glass-ceramics of pure or rare earth-doped B_2O_3 -PbO glasses have attracted special attention due to their potential applications in thermoluminescent dosimetry and solidstate lasers.^{7,8} In addition, lead borate glass matrix owns interesting nonlinear optical properties, being promising materials for all-optical switching and optical limiting devices.⁹ The optical nonlinearities of lead borate glasses are directly related to the PbO content and its crystallization could enhance the material response. Thus, the spatial control of surface crystallization of lead-based glasses is potentially interesting for the development of nonlinear optical microdevices.

> In this study, we report the microcrystal architecture in a borate glass with high-lead content using a combination of DLW and chemical etching at room temperature. Whereas the etching in an aqueous solution of KOH is responsible for the crystallization of lead oxide and lead oxide hydrate phases, the laser writing catalyzes and spatially localizes the growth process in a 2D pattern. Octahedral and sheet-like euhedral microcrystals have been obtained in the laserirradiated area. Because DLW was performed with femtosecond laser pulses, the architecture of the crystals can be achieved in submicrometric regions. In this case, material



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modification occurs only in the focal volume, where the laser intensity is high enough to induce a nonlinear optical process.⁴ The advantage of using laser processing followed by chemical etching is not only its ability to control the crystal architecture, but also the formation of glass-ceramics from amorphous matrixes that do not crystallize by heat treatment, as in the case of $50BO_{1.5}$ -50PbO glass, investigated herein.

Materials and methods

We used anhydrous B₂O₃ (Alfa Aesar, 99.98%) and PbO (Alfa Aesar, 99.99%) as raw materials to prepare the $50BO_{15}$ 50PbO glass (cat%), or 33.33B₂O₃-66.67PbO in mol%, by a melting-quenching technique. Vitreous B₂O₃ was first melted in a platinum crucible at 780 °C for 20 min. PbO was further added, followed by its melt-homogenization for 25 min, and quenching in a stainless-steel mold at 250 °C. The glass was kept at this temperature for 22 h and slowly cooled to room temperature for stress removal. Differential scanning calorimetry (DSC) measurements showed that the glass transition temperature (T_g) is 318 ± 2 °C and no crystalline phase was formed up to the temperature of 1240 °C. Therefore, sample crystallization is not achieved by heat treatment. The absorption edge wavelength of the sample is 395 nm (E_{gap} = 3.14 eV), and there are no electronic transitions in the visible spectrum. The characterization of the third-order optical nonlinearities, including the nonlinear index of refraction and the two-photon absorption coefficient, was thoroughly reported in ref. 9 for the wavelength range from 470-1550 nm.

In order to achieve the microcrystal architecture in 50BO_{1.5}-50PbO glass, DLW was carried out with a femtosecond laser (Ti:sapphire amplified system), operating at 775 nm, with pulses of 150 fs and a repetition rate of 1 kHz. The optical setup is fully described in ref. 5 and basically consists of a microscope objective lens (NA = 0.25 or 0.65) to focus the beam on the sample surface and an xyz stage that moves the sample perpendicularly to the beam at a scan speed of 100 μ m s⁻¹. The crystallization of the laser ablated regions is achieved by chemical etching in an aqueous solution of KOH (concentration ranging from 1 to 5 g L^{-1}) for 3 minutes at room temperature; such etching conditions were revealed to be appropriate for the growth of crystals sized $\sim 6 \ \mu m$. It is worth pointing out that although the crystallization is spatially controlled by the laser, it is a consequence of the chemical etching.

Samples were characterized by: X-ray diffraction, using Cu-K_{α} radiation (Rigaku) with 2 θ angular scan from 20–70° and steps of 0.02°; scanning electron microscopy (Hitachi TM3000); micro-Raman spectroscopy (Witec, Alpha 300), using a HeNe laser as an excitation source, with λ = 632.8 nm and *P* = 8 mW, an objective lens of 100×, an integration time of 4 s and a resolution of 3 cm⁻¹; and Fourier transform infrared (FTIR) spectroscopy from crystallized samples dispersed in KBr wafers (Bruker-Vertex 70).

Results

To control the crystallization in pre-determined regions, the glass sample surface was irradiated with a focused fs-laser beam. Due to the high laser intensity provided by ultrashort laser pulses and a tight focalization, DLW may lead to material ablation. Fig. 1 shows the width of grooves, obtained by fs-laser induced ablation, as a function of the laser pulse energy for four scan speeds, using an objective lens of NA = 0.65. By changing the scan speed and pulse energy, the width of the grooves can be controlled in the range of 2-28 µm. Different from the ablation caused by long pulses, which is dominated by thermal diffusion, at the ultrashort laser pulse regime the thermal effects are minimized and multiphoton, tunneling and avalanche ionizations are the main processes related to material ablation.¹⁰ These interactions are observed in transparent materials even with the ionization potential or bandgap energy (E_{gap}) greater than the photon energy, promoting electrons to the conduction band. When the density of electrons in the conduction band reaches a critical value, ablation takes place as a consequence of plasma formation.¹¹ The behaviour in Fig. 1 is usually described by the logarithmic function $L \approx \alpha^{-1} \ln(E_a/E_{th})$, where L is the ablation width or depth, α^{-1} is the optical penetration depth and $E_{\rm a}$ and $E_{\rm th}$ are the absorbed and threshold laser energies, respectively. By fitting such a function to the data, represented by the solid lines in Fig. 1, we determined a threshold energy of $E_{\rm th} = 0.15 \ \mu J$ (or $F_{\rm th} = 4.8 \ J \ {\rm cm}^{-2}$; $I_{\rm th} = 32 \ {\rm TW} \ {\rm cm}^{-2}$, assuming $w_0 = 1 \ \mu m$ and $\tau = 150 \ fs$), which corresponds to the minimal pulse energy needed to cause material modification.

Grooves sized approximately 5 μ m were produced using twice the threshold energy and then subjected to chemical etching ([1 g L⁻¹]/3 min). Fig. 2 shows the micromachined grooves before (a) and after the etching (b), clearly demonstrating the effect of aqueous KOH solution in the ablated regions. As one can note, the irradiated lines became



Fig. 1 Width of ablated grooves on the surface of $50BO_{1.5}$ -50PbO glass as a function of the pulse energy, for scan speeds ranging from 50-500 μ s, using an objective lens of NA = 0.65. The solid lines represent the fit obtained with the equation given in the text. The threshold energy for material modification is 0.15 μ J.



Fig. 2 Scanning electron microscopy (SEM) images of the glass surface: a) micromachined using $E_{\rm p}$ = 0.3 µJ and 100 µm s⁻¹ and b) after its chemical etching in [1 g L⁻¹] aqueous KOH solution for 3 min, which results in groove crystallization.

crystalline as a consequence of the chemical etching, and two morphologies are observed: octahedral and sheet-like crystals. Differences seen on two consecutive lines in Fig. 2 are due to a mechanical problem in the translational stages, which displace the sample surface regarding the beam focus causing minor variation on the groove size. Fig. 3 (curve 1) displays the X-ray diffraction (XRD) pattern of the ~0.5 cm² area that was subjected to the previous experimental conditions, *i.e.* fs-laser irradiation and further chemical etching ([1 g L⁻¹]/3 min), along with a non-irradiated sample, but etched for 4 h in a [1 g L⁻¹] KOH solution (curve 2).

Both diffractograms contain orthorhombic – PbO (β -PbO or massicot) and tetragonal – 3PbO-H₂O crystalline phases, indexed to JCPDS files #38-1477 and #22-1134, respectively. The broad halos in the diffractogram of curve 1 arise from the amorphous region of the sample between consecutive lines, since only the ablated lines have been crystallized, whereas the procedure without fs-laser micromachining



Fig. 3 X-ray diffraction patterns of 50BO_{1.5}–50PbO glass after (1) fslaser irradiation and further chemical etching using [1 g L⁻¹] aqueous KOH solution for 3 min; and (2) only chemical etching using [1 g L⁻¹] KOH solution for 4 h, without laser irradiation. Both diffractograms contain β -PbO and 3PbO·H₂O crystalline phases.

(curve 2) results in the crystallization of the whole surface. Although it has been reported that laser exposure can result in phase transition,¹² the crystallization of non-irradiated samples can also be achieved by KOH etching, but not under the same conditions used in the irradiated sample. For instance, no significant crystallization was observed when a nonirradiated sample was etched in KOH [1 g L⁻¹] for 3 min, whereas partial crystallization was achieved, for the same etching concentration, after 30 minutes and complete surface crystallization was achieved after 4 h.

In order to associate each one of the morphologies, octahedron and sheet, with the respective crystalline phase, micro-Raman measurements were performed, as shown in Fig. 4. The Raman spectrum of the octahedral crystals presents five sharp peaks: at 160(s), 205(w), 366(m), 428(vw) and 482(vw) cm⁻¹, and a band at ~790 cm⁻¹, while only two peaks are obtained for the sheet morphology, at 287(vs) and 380(w) cm⁻¹. Indexation of the Raman peaks is displayed in Table 1. The FTIR spectrum of the crystallized sample is shown in the inset of Fig. 4 in order to demonstrate the presence of water molecules and hydroxyl groups through the vibrations at 1652 and 3340 cm⁻¹, respectively. The vibrational spectra in Fig. 4 are in agreement with the XRD data, in which 3PbO·H₂O and β-PbO phases were determined and correspond respectively to the octahedral and sheet-like crystals.

Discussion

Lead compounds have been extensively used in the glass industry to obtain low-melting temperature and high refractive index glasses. In addition, technological interest in nonlinear photonics has stimulated the synthesis of Pb-based quantum dots in glassy systems.¹³ There are a number of studies on the crystallization process of lead-based glass motivated by



Fig. 4 Raman spectra of the crystals with octahedral and sheet morphologies, which correspond to 3PbO·H₂O and β -PbO phases, respectively. Excitation was carried out at 514 nm. The inset displays the FTIR spectrum of a crystallized sample dispersed in KBr wafers to demonstrate the presence of HOH and OH vibrations.

Table 1 Attributions of the Raman peaks of lead oxide (β -PbO) and lead oxide hydrate (3PbO·H₂O) crystalline phases associated with sheet and octahedral morphologies

Peak position (cm ⁻¹)	Raman signature	Ref.
Octahedron (3PbO·H ₂ O)		
160vs	Pb–Pb stretching	15
205w	Unassigned	15
366s	Pb–O stretching	15
428w	Pb-O stretching	15
482w	C	This work
790w		This work
Sheet (β-PbO)		
287vs	Motion of O atoms (A _g mode)	16 and 17
380w	Motion of O atoms $(B_{1g} mode)$	16 and 17

the production of glass-ceramics with low-melting temperature and high dielectric permittivity.¹⁴ In such investigations, the precipitation of lead metaborate, lead silicate and lead titanate crystallites is usual; however the crystallization of lead monoxide itself has not been achieved. Although lead oxide compounds are widely studied, very few reports are available for the crystalline phases identified therein. Lead monoxide has two polymorphic forms: i) litharge or red lead (α -PbO) with a tetragonal crystal system, being the most stable structure; and ii) massicot, also called yellow lead or β -PbO, which is orthorhombic. In both polymorphs, Pb²⁺ ions are pyramidally coordinated by oxygen atoms arranged in a layered structure that is stabilized by non-bonding pairs of valence electrons, usually forming crystals in the shape of plates.

Particularly, the structure of massicot is represented by a zigzag chain of 2 [PbO] units repeated parallel to the *b* axis of the cell and layers of these chains stacked along the *a* axis, as illustrated in ref. 17 and 18. β -PbO owns twelve Raman active modes, represented by 4B_{1g}, 2B_{2g}, 2B_{3g} and 2A_g, which are all in phase deformation. Adams and Stevens reported 11 Raman peaks in the experimental spectrum, some of them could be only observed at low temperatures.¹⁷ This spectrum featured the two strongest peaks at 144 and 289 cm⁻¹, in which the former one is not supposed to be fundamental and not seen for the β -PbO crystals obtained herein. Vigouroux *et al.* attributed this peak (144 cm⁻¹) to an interlayer movement involving the Pb²⁺ cations that vibrate perpendicularly to the layers.¹⁹

Similarly, the morphology of octahedral crystals in Fig. 2b matches with the structure of the 3PbO·H₂O phase. The basic structural unit of lead oxide hydrate is described by an octahedron of lead atoms with all eight triangular faces containing an oxygen atom at their centres, giving cubes of oxygen atoms.^{15,20,21} The indexation of 3PbO·H₂O was carefully done due to its similarity with lead-hydroxy complex ions, such as $Pb_3O_2(OH)_2$. The discrimination between water molecules and hydroxyl groups in such compounds is difficult to achieve because the XRD pattern is dominated by the diffraction of lead atoms.²⁰ Also, the scarce literature presents controversial discussions on the description of the structural formula.²⁰⁻²² However, spectroscopic measurements have been shown to be a suitable tool for the identification of hydroxyls and molecular water.^{20,22} FTIR spectroscopy was carried out, and we found the v_2 bending vibration of HOH bonds at 1652 cm⁻¹, which is a fingerprint of molecular water, supporting that the crystalline phase corresponds to lead oxide hydrate instead of lead oxide hydroxide. In addition, the infrared vibrations at 485, 685 and 1384 cm⁻¹ (inset of Fig. 4) were observed in ref. 23 which studied the hydrated forms of lead oxide. Also, the Raman spectrum in Fig. 4 (octahedron) is in agreement with that reported by Cram and Davies, who described 2A1g, 2Eg, 3T2g Raman active modes of 3PbO·H₂O.¹⁵ The region 70-200 cm⁻¹ corresponds to metalmetal stretching and vibrations within $\sim 200-450$ cm⁻¹ are due to metal-oxygen interactions, as presented in Table 1. The spectrum obtained here (Fig. 4) presents a weak peak and a broad band at 482 and \sim 790 cm⁻¹, respectively, not displayed in ref. 15.

It is known that the reaction of lead salts, such as acetate, perchlorate and nitrate, with alkaline solutions results in the formation of lead oxide, as well as lead oxide hydroxide/hydrated compounds.^{24–26} Independent of the laser ablation effect, the crystallization of $50BO_{1.5}$ –50PbO glass is explained based on the lixiviation of the borate matrix by the aqueous KOH solution, resulting in the increase of the concentration of lead-based structural units and lead ions, which subsequently crystallize as lead oxide hydrate and lead oxide. We suppose that the chemical process is accomplished by the formation of boric acid in solution besides the $3PbO \cdot H_2O$ and β -PbO crystalline phases, as described by:

$$4(BO_{1.5}PbO)_{glass} \xrightarrow{KOH \text{ in } H_2O} 4H_3BO_{3(aq.)} + 3PbO \cdot H_2O_{cryst.} + PbO_{cryst.}$$

Thus, the absence of this vibration in our spectrum might be associated with the thin thickness of the crystal, and therefore a small amount of layers. Although there are differences between irreducible representations (mainly between ref. 17 and 19), the observed peaks at 287 and 380 cm⁻¹ are usually described by A_g and B_{1g} modes, respectively, and correspond to the displacement of oxygen atoms. Raman spectra, XRD pattern and SEM analyses demonstrate that the sheet-like crystals correspond to the β -PbO phase and its morphology represents the layered structure of lead monoxide. at room temperature, where O and H atoms are not balanced.

Femtosecond laser micromachined grooves enable euhedral crystals to be obtained, octahedron and sheet, whose morphology corresponds to the structure of $3PbO \cdot H_2O$ and β -PbO phases, respectively. Because the size of the laser ablated lines can be controlled in the range of 2–28 μ m (see Fig. 1), such grooves act as micro-reactors for crystal nucleation and growth,²⁷ since a supersaturated solution of lead ions is confined in these regions due to the increase of



Fig. 5 SEM images demonstrating the spatial control of surface crystallization through the fabrication of a polycrystalline 2D pattern (USP initials) and the isolation of monocrystals.

lixiviation rate. Thus, direct laser writing followed by chemical etching allows not only space-selective crystallization, but also production of isolated microcrystals, as illustrated in Fig. 5.

Even though both phases are concomitants, we noted a predominant accumulation of 3PbO·H2O octahedra within shallow ablated lines, indicating that the crystallization of this phase occurs in the initial stages of nucleation and growth. In fact, shallow lines present more octahedra than deeper lines, which frequently display more of the two morphologies. Thus by keeping the etching conditions and slightly changing the focus position it is possible to grow more octahedral crystals, as shown in Fig. 5. Additionally, by manipulating the chemical etching it is possible to select the crystalline phases, since it has been demonstrated that silica inhibits the formation of anhydrous lead oxide and favors the hydrated one.²⁴ Also, we found out that by using HCl instead of aqueous KOH solution, the laser and etching processes enable the growth and control of PbCl₂ crystallites, with a needle-like morphology (results not shown). Such features demonstrate the versatility of this laser and etching based method to explore other glassy matrixes aiming at controlling the architecture of several crystalline phases. It is worth pointing out that the 50BO_{1.5}-50PbO glass investigated herein does not crystallize via heat treatment, avoiding the preparation of glass ceramics using traditional methods. Moreover, the crystallization of PbB4O7, Pb5B8O17 and Pb₆B₁₀O₂₁ phases in B₂O₃-PbO binary glasses is common,^{8,28} therefore we believe that this is the first report on the controlled crystallization of boron-free phases in such a glassy system.

It is worth emphasizing that crystallization is a process strictly related to the chemical etching of the lead borate glass in alkaline solution. The DLW produces channels which works as micro-reactors, accelerating the crystal growth in the irradiated regions and consequently providing the architecture of micro-crystals. Other methods that result in controlled surface structuring, such as plasma or ion beam etching, would also lead to the architectural control of crystals. However, direct laser writing with fs-laser is advantageous for enabling material processing at the microscale under atmospheric conditions, giving rise to a fast and low-cost method.

Conclusions

We demonstrate the spatial control of surface crystallization of lead borate glass, in which the lead oxide and lead oxide hydrated phases are grown in shape of sheets and octahedral microcrystals, respectively. Such morphologies correspond to the structure of the respective compounds, described by layers of PbO units in the former case (β-PbO) and an octahedron of lead atoms containing a cube of oxygen atoms for the latter one (3PbO·H₂O). Although both phases are crystallized from the glass matrix using only etching in alkaline solution, direct laser writing has enabled the architecture of the microcrystals to be controlled by providing a supersaturated solution of lead ions within the laser ablated grooves, which favors the crystal growth process. Thus, by using femtosecond laser micromachining followed by chemical etching, it is possible not only to control the phase transformation at the micrometer scale, but also to produce a polycrystalline 2D pattern, as well as isolated microcrystals, being an interesting step towards the development of advanced glass-ceramics.

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